

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-329524

(43)Date of publication of application : 15.11.2002

---

(51)Int.Cl. H01M 10/36  
H01B 1/06

---

(21)Application number : 2002-033336

(71)Applicant : SUMITOMO ELECTRIC IND LTD

(22)Date of filing : 12.02.2002

(72)Inventor : HISAGAI YUICHI  
OTA YUKIHIRO

---

(30)Priority

Priority number : 2001053614 Priority date : 28.02.2001 Priority country : JP

---

(54) INORGANIC SOLID ELECTROLYTE AND LITHIUM BATTERY MEMBER

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a sulfide inorganic solid electrolyte restrained from reacting with silicon sulfide even if it is brought into contact with lithium metal and to provide its formation method, a lithium battery member and a lithium secondary battery.

**SOLUTION:** This inorganic solid electrolyte contains 25-60 atom.% of Li, and its remaining part substantially comprises P and S and does not contain Si. In particular, it is desirable that an oxygen quantity is gradually changed from the inorganic solid electrolyte toward a lithium containing material on the boundary between the lithium containing material and the inorganic solid electrolyte in an analysis by XPS capable of keeping an analysis chamber in ultra-high vacuum  $\leq 1.33 \times 10^{-9}$  hPa, and an oxygen containing layer having resided on the surface of the lithium containing material is generally removed. This kind of electrolyte can be realized by superposing a formation process for an inorganic solid electrolyte film on at least a part of a process for etching a base material surface by irradiating inert gas ions on the base material surface.

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1]An inorganic solid electrolyte comprising Li, P, and S substantially and not containing Si.

[Claim 2]The inorganic solid electrolyte according to claim 1 characterized by the remainder comprising P and S substantially below 60 atom % including [ more than 20 atom % ] Li.

[Claim 3]The inorganic solid electrolyte according to claim 1 or 2, wherein said inorganic solid electrolytes are a lithium sulfide ( $\text{Li}_2\text{S}$ ) and a compound of a phosphorus sulfide ( $\text{P}_2\text{S}_5$ ).

[Claim 4]The inorganic solid electrolyte according to any one of claims 1 to 3 characterized by X/Y being 19 or less or more in 1.0 when composition ratio of lithium (Li) is set to X and composition ratio of Lynn (P) is set to Y.

[Claim 5]The inorganic solid electrolyte according to any one of claims 1 to 4, wherein said inorganic solid electrolyte contains either [ at least ] oxygen or nitrogen further.

[Claim 6]The inorganic solid electrolyte according to claim 5, wherein said inorganic solid electrolyte contains one or more of  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{O}$ , and  $\text{P}_2\text{O}_5$ .

[Claim 7]The inorganic solid electrolyte according to any one of claims 1 to 6 in which thickness of said inorganic solid electrolyte is characterized by 0.01-micrometer or more being 10 micrometers or less.

[Claim 8]The inorganic solid electrolyte according to any one of claims 1 to 7, wherein said inorganic solid electrolyte is amorphous.

[Claim 9]A lithium battery member, wherein the inorganic solid electrolyte according to any one of claims 1 to 8 is formed in the surface of a lithium metal or a lithium alloy.

[Claim 10]By analysis by XPS which can be held to an ultrahigh vacuum below  $1.33 \times 10^{-9}$  hPa, a chemical laboratory. The lithium battery member according to claim 9, wherein the amount of oxygen is changing from an inorganic solid electrolyte to a target gradually toward a lithium metal or a lithium alloy on a boundary of a lithium metal or a lithium alloy, and an inorganic solid electrolyte.

[Claim 11]The lithium battery member according to claim 10, wherein a nitride layer intervenes between the surface of a lithium metal or a lithium alloy, and an inorganic solid electrolyte.

[Claim 12]A lithium secondary battery, wherein a negative electrode is the battery member according to any one of claims 9 to 11.

[Claim 13]A formation method of an inorganic solid electrolyte being a formation method of an inorganic solid electrolyte which forms an inorganic solid electrolyte thin film on a substrate, comprising Li, P, and S substantially, heating substrate temperature at not less than 40 \*\* 180 \*\* or less, and forming an inorganic solid electrolyte thin film which does not contain Si.

[Claim 14]It is a formation method of an inorganic solid electrolyte which forms an inorganic solid electrolyte thin film on a substrate, A formation method of an inorganic solid electrolyte by which it is heating [ after forming an inorganic solid electrolyte thin film which is substantially constituted from substrate temperature below 40 \*\* by Li, P, and S, and does not contain Si ]-at not less than 40 \*\* 180 \*\* or less-substrate with which thin film was formed characterized.

[Claim 15]A formation method of the inorganic electrolyte according to claim 13 or 14 characterized by the remainder comprising P and S substantially below 60 atom % including [ more than 20 atom % ] Li.

[Claim 16]A formation method of the inorganic solid electrolyte according to any one of claims 13 to 15 forming an inorganic solid electrolyte thin film by ion plating sputtering process, a vacuum deposition method, a laser ablation method, or the method.

[Claim 17]A formation method of an inorganic solid electrolyte characterized by comprising the following.

A process of irradiating a base material surface with inert gas ion, and etching a base material surface.

A formation process of inorganic solid electrolyte membrane performed by at least a part overlapping with said etching process.

---

[Translation done.]

**\* NOTICES \***

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to an inorganic solid electrolyte and its formation method. It is related with the lithium battery member and lithium secondary battery using this inorganic solid electrolyte.

[0002]

[Description of the Prior Art]Utilization of the lithium secondary battery which uses organic electrolysis liquid is progressing. The place by which it is characterized [ the ] is that unit volume or the energy output per unit weight is high as compared with other cells.

Utilization development is furthered as mobile communications, a notebook computer, or a power supply for electromobles.

[0003]In order to raise the performance of a lithium secondary battery, the trial which is going to use a lithium metal as a negative electrode occurs, but growth of the lithium metal of arborescence takes place on a negative electrode at the time of charge and discharge, an internal short circuit with an anode is caused, and it has the danger of resulting in explosion eventually. As the technique of suppressing this danger, forming the inorganic solid electrolyte thin film of a sulfide system on a lithium metal is examined as indicated to JP,2000-340257,A.

[0004]As a solid electrolyte used for a lithium cell etc., "Solid State Ionics5(1981)663-666", "The electrochemistry 65, No.11 (1997) 914-919", JP,2001-250580,A, "J. Am.Cream.Soc, 84[2]477-79 (2001)", JP,5-48582,B and JP,4-231346,A -- "-- the 26th solids -- Io -- art given in collection (2000) of NIKUSU debate lecture gists 174-175", US No. 6,025,094 gazette, and US No. 5,314,765 gazette is known.

[0005]

[Problem(s) to be Solved by the Invention]However, when the inorganic solid electrolyte thin film of a sulfide system containing a silicon sulfide was contacted to the lithium metal, silicon of the silicon sulfide ( $\text{SiS}_2$ ) was returned by the lithium metal, and it became clear that an inorganic solid electrolyte deteriorated temporally also in a room temperature.

[0006]Generally on the lithium metal, the layer with low ionic conductivity of an oxide etc. is formed, and when this oxide layer exists, the aforementioned lithium metal and the reaction of a silicon sulfide tend to be inhibited. However, in order to improve battery capacity, when the oxide layer was removed, it turned out that temporal deterioration of a lithium metal and the inorganic solid electrolyte accompanying the reaction of a silicon sulfide actualizes.

[0007]Then, even if the key objective of this invention makes a lithium metal contact, there is in providing the battery member and lithium secondary battery using the inorganic solid electrolyte of a sulfide system in which a reaction with a silicon sulfide is inhibited, and that formation method and this inorganic solid electrolyte.

[0008]

[Means for Solving the Problem]A silicon sulfide ( $\text{SiS}_2$ ) reacts to a lithium metal in a room temperature, and this invention is based on knowledge that degradation of an inorganic solid electrolyte arises, and attains the above-mentioned purpose by not making Si contain in an inorganic solid electrolyte.

[0009]<An inorganic solid electrolyte, i.e., this invention inorganic solid electrolyte,> comprises Li, P, and S substantially, and it does not contain Si. It is preferred that the remainder comprises P and S substantially and does not contain Si in particular, below 60 atom % including [ more than 20 atom % ] Li. It is the below 60 atom % hidden remainder's comprising P and S substantially in Li in more than 25. atom %, and not containing Si more

preferably. Inevitable impurities shall be contained in addition to an element made to contain significantly that it is substantial in this invention.

[0010]As for Si, it is desirable to make it not contained in a main skeleton of a glassiness constituent of an inorganic solid electrolyte. Although it was regarded as natural conventionally that Si contains in an inorganic solid electrolyte thin film of a sulfide system, it was not known that this Si will have an adverse effect on performance of an inorganic solid electrolyte, and any measures were not taken, either. So, in this invention, temporal deterioration of a lithium metal and an inorganic solid electrolyte accompanying a reaction of a silicon sulfide is controlled by not including Si. If Si is not included, suppose that content of Si is less than one atom %.

[0011]An inorganic solid electrolyte of a lithium \*\*\*\*- sulfur system which does not contain silicon is excellent for the following reasons compared with other sulfide inorganic solid electrolytes, especially a sulfide inorganic solid electrolyte containing silicon.

[0012]1. Ionic conductivity is high.

2. Even if it makes the lithium metal surface contact, don't cause a reaction with a lithium metal like a sulfide inorganic solid electrolyte containing silicon.

3. In a lithium secondary battery using organic electrolysis liquid of non-water, when an inorganic solid electrolyte is formed on a lithium metal and it is considered as a negative electrode, it has the following characteristic.

- Depressor effect of dendritic growth is excellent.

- Chemical stability over an electrolysis solution is excellent.

- A mechanical strength is strong to morphology change in a charging and discharging cycle.

4. Although  $\text{SiS}_2$  is expensive, price of a phosphorus sulfide ( $\text{P}_2\text{S}_5$ ) is also comparatively cheap, and since it is easy to receive, it is suitable for industrial production.

[0013]As for lithium-elements content in this inorganic electrolyte layer, below 60 atom % carries out above 20 atom %. By less than 20 atom %, ionic conductivity becomes low and high-resistance-izes. The adhesion of an inorganic solid electrolyte layer and a lithium metal layer falls. although the adhesion of an inorganic solid electrolyte layer and a lithium metal layer will improve on the other hand if 60 atom % is exceeded -- an inorganic solid electrolyte layer -- polycrystal-izing -- and it porosity-izes and formation of a continuation film of a precise inorganic solid electrolyte becomes difficult. Moreover, electron conductivity is revealed, when a cell is constituted, an internal short circuit is caused, and battery capacity is reduced. Therefore, as for an electrolyte layer, it is preferred that they are amorphous bodies. In this invention, it is substantially formed with an amorphous substance (glass) that it is amorphous, When becoming a halo pattern by an X diffraction, of course, a case where few peaks by a starting material, output, etc. are seen in addition to a halo pattern, and a case where a peak of a substrate (at the time of thin film forming) is seen (when a crystal grain of a starting material or output deposits in part) shall be included.

[0014]Below 20 atom % of phosphorus element content is [ more than three atom % ] preferred. Below 60 atom % of sulfur elemental content is [ more than 30 atom % ] preferred. If there is little content of Lynn or sulfur, it will become easy to generate a defect. If there are much Lynn and sulfur, the Lynn simple substances and sulfur simple substances as an impurity will increase in number in a solid electrolyte.

[0015]As a concrete compound contained in this invention inorganic solid electrolyte, a lithium sulfide ( $\text{Li}_2\text{S}$ ) and a compound of a phosphorus sulfide ( $\text{P}_2\text{S}_5$ ) are preferred. When composition ratio of lithium (Li) is set to X and composition ratio of Lynn (P) is especially set to Y, it is preferred that X/Y is 19 or less [ 1.0 or more ].

[0016]In this inorganic solid electrolyte, either [ at least ] oxygen or nitrogen may contain. Content of oxygen or nitrogen minute amount [ below / a pentatomic % grade ] enables it to demonstrate still higher lithium ion conductivity. An effect which extends a crevice between amorphous skeletons formed is brought about, and this is presumed because hindrance which a lithium ion moves is reduced, when very small quantity oxygen atom or nitrogen atom contains.

[0017] $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ , etc. are mentioned as a compound containing oxygen. As a compound containing nitrogen,  $\text{Li}_3\text{PO}_{4-X}\text{N}_{2X/3}$  ( $0 < X < 4$ ) is mentioned.

[0018]As for such an inorganic solid electrolyte, it is desirable to use a thin film. As for thickness of a thin film, 0.01 micrometers or more 10 micrometers or less are desirable, and it is 0.05 micrometers or more 1 micrometer or less more preferably. This is for a defect of a pinhole etc. to increase, if too thin, for process time to become long and for a manufacturing cost to increase, if too thick.

[0019]<Lithium battery member> As for the above-mentioned inorganic solid electrolyte, it is desirable to form in

the surface of a lithium metal or a lithium alloy (lithium content material) so that it can use as a battery member. As an example of a lithium alloy, an alloy with Li, In, Ti, Zn, Bi, or Sn is mentioned.

[0020]Metal thin films, such as metal which forms lithium, an alloy, or an intermetallic compound in the surface of this lithium content material, for example, aluminum, In, Bi, Zn, and Pb, may be formed. By using a negative electrode which consists of this metal thin film and lithium content material, movement of a lithium metal at the time of charge and discharge becomes smooth, and use thickness of a lithium metal increases. Modification of a negative electrode at the time of charge and discharge becomes uniform, and distortion to an electrolyte layer can be reduced.

[0021]The above-mentioned lithium content material may be used as it is, without performing any pretreatment, when forming an electrolyte layer. However, generally on the surface of a lithium metal, oxide layers ( $\text{Li}_2\text{O}$  etc.), a carbonic acid ghost layer ( $\text{Li}_2\text{CO}_3$ ), a hydroxide layer ( $\text{LiOH}$ ), etc. are formed thinly in many cases. Since such lithium ion conductivity is low, removing is desirable. Removal of an oxide layer etc. can be performed by irradiating with inert gas ion, such as an argon ion beam. As for argon gas used in that case, what has purity high as much as possible is desirable. For example, argon whose purity is 99.9999% is preferred.

[0022]Thereby, an inorganic solid electrolyte thin film can be formed on direct lithium content material, and impedance of lithium content material and an inorganic solid electrolyte layer can be reduced more.

[0023]It is desirable to overlap and to perform a process of irradiating a base material surface with inert gas ion, and etching a base material surface especially, and a formation process of inorganic solid electrolyte membrane. By such membrane formation, analysis by XPS which can hold a chemical laboratory to an ultrahigh vacuum below  $1.33 \times 10^{-9}$  hPa ( $1 \times 10^{-9}$  Torr) on a boundary of lithium content material and an inorganic solid electrolyte. The amount of oxygen can change from an inorganic solid electrolyte to a target gradually toward lithium content material, and an oxide layer which exists in the surface of lithium content material can obtain a lithium battery member removed mostly. 5400 types by the phi company are mentioned as XPS (X-ray Photo-electronic Spectroscopy: X-ray-photoelectron-spectroscopy analysis apparatus) which can hold a chemical laboratory to an ultrahigh vacuum below  $1.33 \times 10^{-9}$  hPa ( $1 \times 10^{-9}$  Torr).

[0024]A ultimate vacuum conventionally by formation of an electrolyte membrane using the usual vacuum devices which are  $1.3 \times 10^{-7}$  hPa ( $1 \times 10^{-7}$  Torr) grades. If a formation process of an electrolyte thin film is performed after performing an etching process, oxygen contained layers (an oxide layer, a carbonic acid ghost layer, a hydroxide layer, etc.) will be easy to be formed between lithium content material and an inorganic solid electrolyte. In this invention, by carrying out by overlapping an etching process and a formation process of an electrolyte thin film, the usual vacuum devices can also eliminate an oxygen contained layer mostly, and can form membranes.

[0025]Although an etching process and a formation process of an electrolyte thin film may overlap thoroughly, it is preferred to overlap selectively the start side of an electrolyte thin film formation process the end side of an etching process. An etching process removes mostly an oxygen contained layer of a base material surface part, and formation of an electrolyte thin film is started in the state where an oxygen contained layer cannot be formed following etching of a base material surface. An electrolyte thin film will be formed in that case, being removed a little by inert gas ion.

[0026]The time to perform an etching process independently should just make an oxygen contained layer of a base material surface part a mostly removable grade. A base material surface should just make time in which an etching process and an electrolyte thin film formation process are overlapped a grade covered with electrolyte thin film material.

[0027]On the other hand, after removing an oxygen contained layer mostly, and forming nitride layers, such as lithium nitride ( $\text{Li}_3\text{N}$ ), an electrolyte thin film may be formed. Ionic conductivity is more than  $1 \times 10^{-3}$  S/cm at a room temperature, and even if  $\text{Li}_3\text{N}$  exists in the middle of a lithium metal and an inorganic solid electrolyte thin film, it does not lead to a fall of current density which can be passed. When a nitride layer exists, generation control of an oxide layer etc. is also expectable.

[0028]Mixed ion beam processing of argon and nitrogen etc. can perform formation of a nitride layer. Thickness of a nitride layer of 1 nm or more is preferred so that it may not be dotted with a portion [ nitriding / a portion / if formed very much only in the surface, is enough, and ] of lithium content material. However, if a nitride layer is too thick, problems, such as a fall of ionic conductivity by polycrystal-izing, a reaction with an electrolysis solution, and degradation of withstand voltage nature, will come out. Therefore, as for thickness of a nitride layer,

it is desirable to use below 0.1 micrometer (100 nm), and it is 10 nm or less more preferably.

[0029]<Lithium secondary battery> The above battery members can be used as a negative electrode of a lithium secondary battery. For example, an anode, a porous separator, and a negative electrode are laminated, organic electrolysis liquid of non-water is impregnated, and a lithium secondary battery can consist of storing and obturating this layered product to a cell case. If it explains to details more, a negative electrode will be first joined to a negative pole collector, a solid electrolyte thin film of an inorganic system which does not contain organic electrolysis liquid will be formed on lithium content material used as a negative electrode, and a zygote of a negative electrode and an electrolyte will be produced. A positive electrode material containing an organic high polymer is formed on a positive pole collector (for example, copper or aluminum foil), and it is considered as an anode. An aforementioned zygote and an anode are intervened and united in a separator, and a lithium secondary battery is produced. Thereby, contact resistance of a negative electrode and an anode, and an electrolyte layer can be reduced, and it becomes possible to acquire a good charging and discharging characteristic. What was made cylindrical may be used by laminating and rolling a negative electrode, an electrolyte layer, and an anode besides a button type battery laminated in this way.

[0030]As construction material of a separator arranged between an anode and a solid electrolyte layer, it has fine pores which a lithium ion can move, and what was insoluble and was stabilized in organic electrolysis liquid is used. For example, a nonwoven fabric and a porous material which were formed from polypropylene, polyethylene, a fluoro-resin, polyamide resin, etc. can be used. In addition, a metallic-oxide film etc. which have fine pores may be sufficient.

[0031]A formation method of a <formation method of inorganic solid electrolyte> this invention inorganic solid electrolyte. It is a formation method of an inorganic solid electrolyte which forms an inorganic solid electrolyte thin film on a substrate, and it comprises Li, P, and S substantially, heating substrate temperature at not less than 40 \*\* 180 \*\* or less, and an inorganic solid electrolyte thin film which does not contain Si is formed. Or after forming the same inorganic solid electrolyte thin film as the above at substrate temperature below 40 \*\*, a substrate with which a thin film was formed is heated at not less than 40 \*\* 180 \*\* or less. It is preferred that the remainder comprises P and S substantially especially, below 60 atom % including [ more than 20 atom % ] Li. It is the below 60 atom % hidden remainder's comprising P and S substantially in Li in more than 25 atom %, and not containing Si more preferably. Thus, when forming an inorganic solid electrolyte thin film, after heating a substrate or forming at a room temperature, a thin film with high ionic conductivity is obtained by heat-treating a thin film. If an inorganic solid electrolyte is formed, or it heat-treats, heating a substrate after forming an inorganic solid electrolyte when forming in the surface of lithium content material an inorganic solid electrolyte containing Si, a reaction of Li and Si will be promoted. On the other hand, if the above heat-treatment is performed when forming in the surface of lithium content material an inorganic solid electrolyte which does not contain Si like this invention, the characteristics, such as ionic conductivity, can form a good inorganic solid electrolyte, and are very effective. When forming an inorganic solid electrolyte thin film, heating a substrate, effects, like the adhesion of a thin film and a substrate becomes good can also be expected.

[0032]It is preferred to perform formation of the above-mentioned inorganic solid electrolyte thin film by ion plating sputtering process, a vacuum deposition method, a laser ablation method, or the method.

[0033]

[Embodiment of the Invention]Hereafter, an embodiment of the invention is described.

(Example 1) At 10 micrometers in thickness, a 10-micrometer-thick lithium metal thin film is formed with a vacuum deposition method on copper foil (100 mm x 50 mm), and an inorganic solid electrolyte thin film is formed on the surface. Instead of a lithium metal thin film, 30-micrometer-thick lithium metal foil can be pasted together in the same size as copper foil, and an inorganic solid electrolyte thin film can also be formed on the lithium metal foil.

[0034]The substrate in which this lithium-metal-foil film was formed is installed in a vacuum film formation apparatus. The ultimate vacuum of vacuum devices is  $5.3 \times 10^{-7}$  hPa ( $4 \times 10^{-7}$  Torr). First, argon gas (99.9999% of purity) is passed so that it may become pressure  $2.7 \times 10^{-4}$  hPa ( $2 \times 10^{-4}$  Torr), and a specimen surface is irradiated with an ion beam for 30 seconds by 15 mA and 500V by ion guns. Membrane formation of an inorganic solid electrolyte is started with a laser ablation method, without interrupting this ion beam irradiation. That is, although ion beam irradiation is continuously performed for 40 seconds, it overlaps with membrane formation of an inorganic solid electrolyte for 10 seconds of the second half, and it is performed. 30 seconds of the beginning are for removal of the oxide layer on a lithium metal, a carbonic acid ghost layer, etc.

[0035] Ion beam irradiation is interrupted, and if membrane formation is started after setting between, in the common vacuum devices whose ultimate vacuum is a  $1.3 \times 10^{-7}$  hPa ( $1 \times 10^{-7}$  Torr) grade, a very thin oxide layer will tend to be generated by the lithium metal surface by the oxygen which remains in a vacuum housing. Therefore, in 10 seconds of the second half, it carries out simultaneous [ion beam irradiation and membrane formation], and an oxide layer is hardly formed and is making.

[0036] After the ion beam stop, membrane formation is continued, and the argon gas pressure was gone up within 3 minutes, and it raised  $2.7 \times 10^{-4}$  hPa ( $2 \times 10^{-3}$  Torr) and temperature at 140 °C from the room temperature. The inorganic solid electrolyte was formed in 0.5 micrometer in thickness on this condition. The laser used for membrane formation is a KrF excimer laser, and laser oscillation frequency was 5 Hz.

[0037] The ion-beam-irradiation conditions (current, time, gas pressure) shown this time are only examples, and it is necessary to adjust them according to the distance etc. of the thickness and ion guns currently formed in the lithium metal surface, such as an oxide layer and a carbonic acid ghost layer, and a sample.

[0038] If the ultrahigh vacuum below  $1.33 \times 10^{-9}$  hPa ( $1 \times 10^{-9}$  Torr) can be reached and adsorption of oxygen inside a container or moisture uses very little vacuum devices, It seems that inorganic solid electrolyte membrane can be formed so that an oxide layer etc. may hardly exist in the lithium metal surface even if after ion beam irradiation and between are set and it starts membrane formation. However, since device cost became very high even if made to producing such a device by requiring very advanced art, the method shown above was adopted.

[0039] The sample A which targets  $63\text{Li}_2\text{S}-36.5\text{SiS}_2-0.5\text{Li}_3\text{PO}_4$  (a numerical value is a mole ratio) in which an inorganic solid electrolyte contains Si. Two kinds of the samples B which target  $78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$  (a numerical value is a mole ratio) which does not contain Si were produced.

[0040] When it took out after membrane formation and the sample was observed, the thin film of the sample A which targeted  $63\text{Li}_2\text{S}-36.5\text{SiS}_2-0.5\text{Li}_3\text{PO}_4$  containing Si had deteriorated deep-black. Usually, the good  $\text{Li}_2\text{S}-\text{SiS}_2$  system thin film is water-white. Ionic conductivity was below  $1 \times 10^{-4}$  S/cm at 25 °C, by carrying out direct

contact to a lithium metal, it reacted to Si and it became clear that it had deteriorated. This ionic conductivity measured the conductivity of the direction vertical to a film surface with the direct-current measuring method.

[0041] On the other hand, the thin film of the sample B which targeted  $78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$  was water-white, and when ionic conductivity was measured, it was  $1.3 \times 10^{-3}$  S/cm at 25 °C. Ionic conductivity was measured like the sample A. Li composition ratio (atomic %) of this sample B was 41% as a result of EPMA (ElectronProbe Micro Analyzer) analysis. The presentation (atomic %) of a thin film is measured by the above-mentioned EPMA, XPS, ICP (Inductively Coupled Plasma) spectrographic analysis, the gas analysis by inert-gas-fusion infrared absorption spectrometry, etc. the ratio which analyzed the thin film formed on the glass substrate by the same film formation condition as the sample B by ICP, asked for the composition ratio X of Li, and the composition ratio Y of P, and was calculated after this — X/Y was 3.6. The ICP analysis apparatus used at this time is a SEIKO electronic company make SPS1200VR type. In the X diffraction, it was checked except the peak from a substrate that it is only a very small peak and the sample B is an amorphous state.

[0042] Furthermore, A chemical laboratory.  $1.33 \times 10^{-9}$  hPa. ( $1 \times 10^{-9}$  Torr) The component analysis in a lithium metal thin film was conducted from inorganic solid electrolyte membrane using XPS (X-ray Photo-electronic Spectroscopy: X-ray-photoelectron-spectroscopy analysis apparatus) which can be held to the following ultrahigh vacuums. The devices used for analysis are the 5400 types by the phi company. The result checked what the amount of oxygen is changing from the inorganic solid electrolyte to the target gradually toward a lithium metal thin film on the boundary with a lithium metal thin film (it is decreasing) from inorganic solid electrolyte membrane. Before forming inorganic solid electrolyte membrane, it was checked that the oxide layer which exists in the lithium metal surface has removed mostly.

[0043] The substrate in which the inorganic solid electrolyte thin film which targets  $78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$  was formed on the lithium metal thin film is used as a negative electrode, The lithium secondary battery which consists of a separator (porosity polymer film), an anode, organic electrolysis liquid, etc. was produced. Below, the production procedures and cell evaluation result of a cell are described.

[0044] The mixed solution of ethylene carbonate (EC) and propylene carbonate (PC) was heated, what dissolved polyacrylonitrile (PAN) in high concentration was cooled, and EC which  $\text{LiPF}_6$  is dissolving, and PAN which contains PC so much were produced. Into this PAN, the  $\text{LiCoO}_2$  particles used as an active material and the



carbon particle for which electron conductivity is given were mixed, and it applied by a thickness of 300 micrometers on the aluminum foil (positive pole collector) of 20-micrometer thickness, and was considered as the anode.

[0045]The negative electrode, the separator (porosity polymer film) in which the solid electrolyte thin film was formed, And install an anode in piles into the hermetic container made from stainless steel, and the organic electrolysis liquid made to dissolve 1-mol% of  $\text{LiPF}_6$  in the mixed solution of ethylene carbonate and propylene carbonate as an electrolysis salt further is dropped, The lithium secondary battery was produced under the argon gas atmosphere not more than dew point-60 \*\*.

[0046]The charging and discharging characteristic of the produced cell was evaluated. As a result, capacity until any cell sets charge voltages to 4.2V and voltage falls to 3.0V by 100-mA discharge was 0.5Ah (amp-hr). Energy densities were 500Wh(watt-hour) /1 (liter).

[0047]The cycle charge and discharge of the still more nearly same conditions were performed. It is stable in 600 times or more of cycles, and not less than 50% of initial capacity was maintaining also after 600 times of cycles.

[0048](Example 2) The 10-micrometer-thick lithium metal thin film was formed with the vacuum deposition method on copper foil (100 mm x 50 mm) at 10 micrometers in thickness. On this lithium metal thin film, the 0.5-micrometer-thick inorganic solid electrolyte thin film was formed. It is the same as that of Example 1 that lithium metal foil may be pasted together to copper foil.

[0049]The substrate in which this lithium metal thin film was formed was installed in vacuum devices, and ion beam processing was performed first. Argon of pressure  $2.7 \times 10^{-4}$  hPa ( $2 \times 10^{-4}$  Torr) and the mixed gas (argon 75vol.%, nitrogen 25vol.%) of nitrogen were passed, and the specimen surface was irradiated with the ion beam by 15 mA and 500V by ion guns. Below 50vol.% of the nitrogen content of mixed gas is [ more than 10vol.% ] desirable. When large [ when there is little content of nitrogen, the nitriding effect is small, and ], it is because degradation of the filament of ion guns is remarkable. The thickness of the formed nitride layer was 1 nm as a result of analysis by XPS.

[0050]Here, although etching and nitriding treatment of an oxide layer etc. were simultaneously performed using argon nitrogen mixed gas, after only argon gas performs only etching processes, such as an oxide layer, it is also possible to form nitriding thin films, such as lithium nitride, by a gaseous phase method etc. It is also possible to make membrane formation of a nitride layer start in the second half of ion beam irradiation, and to carry out synchronization of the etching process by an ion beam and the membrane formation of a nitride layer.

[0051]And the inorganic solid electrolyte thin film was formed. The formation condition is shown in Table 1 and Table 2. When membranes are formed at a room temperature, without heating a substrate during thin film forming, heat-treatment for 15 minutes is performed at the temperature shown in Table 2 in the Ar gas of atmospheric pressure. the ratio which asked for the composition ratio (atomic %) of Li of the obtained inorganic solid electrolyte thin film, and the ionic conductivity at 25 \*\*, the composition ratio X of Li and the composition ratio Y of P, and was calculated after this -- X/Y (in front, it is indicated as a Li/P ratio) was also calculated. the composition ratio of Li -- analysis of EPMA -- a ratio -- X/Y was calculated by analysis of ICP. ICP analysis analyzed the thin film which formed membranes to a glass substrate or silicon on sapphire by the same film formation condition. These are also collectively shown in Tables 1 and 2. Except for No.2-2 and No.2-8, the composition ratio (atomic %) of S was [ all composition ratios (atomic %) of P / more than three atom % / more than 30 atom % ] contained [ below 20 atom % ] in within the limits below 60 atom %.

[0052]

[Table 1]

No	成膜手法	無機固体電解質薄膜の原料 (モル比)	Li 組成比 (原子%)	Li/P 比
2-1	真空蒸着	$78\text{Li}_2\text{S}-22\text{P}_2\text{S}_5$	40	3.5
2-2	真空蒸着	$96.5\text{Li}_2\text{S}-3\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	62	32
2-3	真空蒸着	$94.5\text{Li}_2\text{S}-5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	60	19
2-4	真空蒸着	$85\text{Li}_2\text{S}-14.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	48	5.9
2-5	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	41	3.6
2-6	真空蒸着	$65\text{Li}_2\text{S}-34.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	30	1.9
2-7	真空蒸着	$60\text{Li}_2\text{S}-39.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	27	1.5
2-8	真空蒸着	$48.0\text{Li}_2\text{S}-51.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	19	0.9
2-9	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_2\text{SO}_4$	41	3.6
2-10	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5(\text{Li}_2\text{O}-\text{P}_2\text{O}_5)$	41	3.6
2-11	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4\cdot\text{NO.1}$	41	3.6
2-12	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	41	3.6
2-13	真空蒸着	$78\text{Li}_2\text{S}-21.9\text{P}_2\text{S}_5-0.1\text{Li}_3\text{PO}_4$	40	3.6
2-14	真空蒸着	$78\text{Li}_2\text{S}-21\text{P}_2\text{S}_5-1\text{Li}_3\text{PO}_4$	41	3.7
2-15	真空蒸着	$75\text{Li}_2\text{S}-20\text{P}_2\text{S}_5-5\text{Li}_3\text{PO}_4$	43	3.8
2-16	スパッタリング	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	41	3.6
2-17	レーザーアブレーション	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	41	3.6
2-18	イオンブレーティング	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	41	3.6
2-19	レーザーアブレーション	$75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$	38	3.0
2-20	レーザーアブレーション	$75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$	38	3.0

[0053]

[Table 2]

No	成膜温度 ℃	成膜後熱処理温度 ℃	イオン伝導度 (25℃) S/cm	リチウム 2 次電池形成時の 充放電安定サイクル数
2-1	140	熱処理なし	$1.3 \times 10^{-3}$	600 以上
2-2	140	熱処理なし	$1.0 \times 10^{-3}$	450
2-3	140	熱処理なし	$1.3 \times 10^{-3}$	600 以上
2-4	140	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-5	140	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-6	140	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-7	140	熱処理なし	$1.3 \times 10^{-3}$	600 以上
2-8	140	熱処理なし	$1.0 \times 10^{-3}$	480
2-9	140	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-10	140	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-11	140	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-12	室温 (25℃)	150	$1.5 \times 10^{-3}$	600 以上
2-13	140	熱処理なし	$1.4 \times 10^{-3}$	600 以上
2-14	140	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-15	140	熱処理なし	$1.4 \times 10^{-3}$	600 以上
2-16	130	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-17	130	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-18	室温 (25℃)	150	$1.5 \times 10^{-3}$	600 以上
2-19	170	熱処理なし	$1.5 \times 10^{-3}$	600 以上
2-20	室温 (25℃)	170	$1.4 \times 10^{-3}$	600 以上

[0054]The lithium secondary battery which consists of a separator (porosity polymer film), an anode, organic electrolysis liquid, etc. was produced by the same method as Example 1 by using as a negative electrode the substrate in which the inorganic solid electrolyte thin film was formed on this lithium metal thin film.

[0055]Capacity as a result of evaluating the charging and discharging characteristic of the produced cell, until any cell sets charge voltages to 4.2V and voltage falls to 3.0V by 100-mA discharge was 0.5Ah (amp-hr). Energy densities were 450-550Wh(watt-hour) /1 (liter).

[0056]The cycle charge and discharge of the still more nearly same conditions were performed. No.2-2 with many amounts of Li(s) and the amount of Li(s) were maintaining 50% of initial capacity also after a 600 times cycle by 600 cycle stability or more except for little No.2-8.

[0057](Example 3) The solid electrolyte thin film was produced on the lithium metal like No.2-5 of Example 2, and

production evaluation of the lithium secondary battery was performed further. This example estimated by changing the thickness of a nitride layer. The result is shown in Table 3.

[0058]

[Table 3]

No	成膜手法	無機固体電解質薄膜の原料 (モル比)	イオン- $\Delta$ 処理	窒化層 の厚さ	成膜温度 ℃	リチウム2次電池 形成時の充放電 安定サイクル数
3-0	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	イオン- $\Delta$ 処理なし	なし	140	510
3-1	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴンイオン- $\Delta$ 照射	なし	140	590
3-2	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン- $\Delta$ 照射	1nm	140	600以上
3-3	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン- $\Delta$ 照射	5nm	140	600以上
3-4	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン- $\Delta$ 照射	10nm	140	600以上
3-5	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン- $\Delta$ 照射	50nm	140	570
3-6	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン- $\Delta$ 照射	100nm	140	520
3-7	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン- $\Delta$ 照射	200nm	140	450

[0059]As for the thickness of a nitride layer, 1 nm or more 100 nm or less is preferred, and it is 1 nm or more 10 nm or less more preferably so that more clearly than Table 3.

[0060]After No.3-1 removed an oxide, a carbonic acid ghost layer, etc. by the argon ion beam in Example 1, when between is set and membranes are formed, it corresponds.

[0061](Example 4) The inorganic solid electrolyte thin film was produced on the same lithium metal thin film as Example 2, and production evaluation of the lithium secondary battery was performed further. In this example, the argon gas of 99.9999% of purity was used instead of the argon nitrogen mixed gas used in Example 2, the etching process was performed, the solid-electrolyte membrane was formed after etching and formation of the nitride layer was not performed. the ratio which asked for the composition ratio (atomic %) of Li of the obtained inorganic solid electrolyte thin film, and the ionic conductivity at 25 \*\*, the composition ratio X of Li and the composition ratio Y of P, and was calculated after this -- X/Y was also calculated. Table 4 and Table 5 -- formation conditions, ionic conductivity, and a ratio -- X/Y (the inside of front Li/P ratio) is shown.

[0062]

[Table 4]

No	成膜手法	無機固体電解質薄膜の原料 (モル比)	Li 組成比 (原子%)	Li/P 比
4-1	レーザーアブレーション	$75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$	38	3.0
4-2	レーザーアブレーション	$75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$	37	2.9
4-3	レーザーアブレーション	$70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$	33	2.5
4-4	レーザーアブレーション	$70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$	34	2.6
4-5	スパッタリング	$80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$	42	4.0
4-6	イオンプレーティング	$80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$	41	3.9
4-7	真空蒸着	$70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$	30	2.3

[0063]

[Table 5]

No	成膜温度 ℃	成膜後熱処理温度 ℃	イオン伝導度(25℃) S/cm	リチウム2次電池形成時の 充放電安定サイクル数
4-1	160	熱処理なし	$3.0 \times 10^{-4}$	500以上
4-2	室温(25℃)	160	$2.5 \times 10^{-4}$	500以上
4-3	170	熱処理なし	$3.5 \times 10^{-4}$	500以上
4-4	室温(25℃)	170	$4.0 \times 10^{-4}$	500以上
4-5	165	熱処理なし	$2.0 \times 10^{-4}$	500以上
4-6	165	熱処理なし	$3.0 \times 10^{-4}$	500以上
4-7	165	熱処理なし	$3.0 \times 10^{-4}$	500以上

[0064]As shown in Table 5, as for any sample, the ionic conductivity more than  $1 \times 10^{-4}$  S/cm was obtained. The component analysis in a lithium metal thin film was conducted from inorganic solid electrolyte membrane using the same XPS as Example 1. The result checked that the amount of oxygen was changing from the inorganic solid electrolyte to the target gradually toward a lithium metal thin film on the boundary with a lithium metal thin film from inorganic solid electrolyte membrane. And before forming inorganic solid electrolyte membrane, it was

checked that the oxide layer which exists in the lithium metal surface has removed mostly. Cycle discharge was performed on the same conditions as Example 2. As a result, as shown in Table 5, it is stable in 500 times or more of cycles, and not less than 50% of initial capacity was maintaining also after 500 times of cycles.

[0065]

[Effect of the Invention]As explained above, according to this invention inorganic solid electrolyte, degradation of the electrolyte membrane by the reaction of a lithium metal and a silicon sulfide can be controlled by not making Si contain. The oxygen contained layer which formed the electrolyte membrane directly on lithium content metal, and existed in the lithium content surface of metal between lithium content metal and an electrolyte membrane especially by removing nearly thoroughly. Resistance of the interface between an electrolyte membrane and lithium content metal is lowered, and high ionic conductivity is realizable.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

TECHNICAL FIELD

---

[Field of the Invention]This invention relates to an inorganic solid electrolyte and its formation method. It is related with the lithium battery member and lithium secondary battery using this inorganic solid electrolyte.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

PRIOR ART

---

[Description of the Prior Art]Utilization of the lithium secondary battery which uses organic electrolysis liquid is progressing. The place by which it is characterized [ the ] is that unit volume or the energy output per unit weight is high as compared with other cells.  
Utilization development is furthered as mobile communications, a notebook computer, or a power supply for electromobiles.

[0003]In order to raise the performance of a lithium secondary battery, the trial which is going to use a lithium metal as a negative electrode occurs, but growth of the lithium metal of arborescence takes place on a negative electrode at the time of charge and discharge, an internal short circuit with an anode is caused, and it has the danger of resulting in explosion eventually. As the technique of suppressing this danger, forming the inorganic solid electrolyte thin film of a sulfide system on a lithium metal is examined as indicated to JP,2000-340257,A.  
[0004]As a solid electrolyte used for a lithium cell etc., "Solid State Ionics5(1981)663-666", "The electrochemistry 65, No.11 (1997) 914-919", JP,2001-250580,A, "J. Am.Cream.Soc, 84[2]477-79 (2001)", JP,5-48582,B and JP,4-231346,A -- "-- the 26th solids -- lo -- art given in collection (2000) of NIKUSU debate lecture gists 174-175", US No. 6,025,094 gazette, and US No. 5,314,765 gazette is known.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

## EFFECT OF THE INVENTION

---

[Effect of the Invention]As explained above, according to this invention inorganic solid electrolyte, degradation of the electrolyte membrane by the reaction of a lithium metal and a silicon sulfide can be controlled by not making Si contain. The oxygen contained layer which formed the electrolyte membrane directly on lithium content metal, and existed in the lithium content surface of metal between lithium content metal and an electrolyte membrane especially by removing nearly thoroughly. Resistance of the interface between an electrolyte membrane and lithium content metal is lowered, and high ionic conductivity is realizable.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**TECHNICAL PROBLEM**

---

[Problem(s) to be Solved by the Invention]However, when the inorganic solid electrolyte thin film of a sulfide system containing a silicon sulfide was contacted to the lithium metal, silicon of the silicon sulfide ( $\text{SiS}_2$ ) was returned by the lithium metal, and it became clear that an inorganic solid electrolyte deteriorated temporally also in a room temperature.

[0006]Generally on the lithium metal, the layer with low ionic conductivity of an oxide etc. is formed, and when this oxide layer exists, the aforementioned lithium metal and the reaction of a silicon sulfide tend to be inhibited. However, in order to improve battery capacity, when the oxide layer was removed, it turned out that temporal deterioration of a lithium metal and the inorganic solid electrolyte accompanying the reaction of a silicon sulfide actualizes.

[0007]Then, even if the key objective of this invention makes a lithium metal contact, there is in providing the battery member and lithium secondary battery using the inorganic solid electrolyte of a sulfide system in which a reaction with a silicon sulfide is inhibited, and that formation method and this inorganic solid electrolyte.

---

[Translation done.]



## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## MEANS

[Means for Solving the Problem]A silicon sulfide ( $\text{SiS}_2$ ) reacts to a lithium metal in a room temperature, and this invention is based on knowledge that degradation of an inorganic solid electrolyte arises, and attains the above-mentioned purpose by not making Si contain in an inorganic solid electrolyte.

[0009]<An inorganic solid electrolyte, i.e., this invention inorganic solid electrolyte,> comprises Li, P, and S substantially, and it does not contain Si. It is preferred that the remainder comprises P and S substantially and does not contain Si in particular, below 60 atom % including [ more than 20 atom % ] Li. It is the below 60 atom % hidden remainder's comprising P and S substantially in Li in more than 25 atom %, and not containing Si more preferably. Inevitable impurities shall be contained in addition to an element made to contain significantly that it is substantial in this invention.

[0010]As for Si, it is desirable to make it not contained in a main skeleton of a glassiness constituent of an inorganic solid electrolyte. Although it was regarded as natural conventionally that Si contains in an inorganic solid electrolyte thin film of a sulfide system, it was not known that this Si will have an adverse effect on performance of an inorganic solid electrolyte, and any measures were not taken, either. So, in this invention, temporal deterioration of a lithium metal and an inorganic solid electrolyte accompanying a reaction of a silicon sulfide is controlled by not including Si. If Si is not included, suppose that content of Si is less than one atom %.

[0011]An inorganic solid electrolyte of a lithium \*\*\*\*- sulfur system which does not contain silicon is excellent for the following reasons compared with other sulfide inorganic solid electrolytes, especially a sulfide inorganic solid electrolyte containing silicon.

[0012]1. Ionic conductivity is high.

2. Even if it makes the lithium metal surface contact, don't cause a reaction with a lithium metal like a sulfide inorganic solid electrolyte containing silicon.

3. In a lithium secondary battery using organic electrolysis liquid of non-water, when an inorganic solid electrolyte is formed on a lithium metal and it is considered as a negative electrode, it has the following characteristic.

- Depressor effect of dendritic growth is excellent.
- Chemical stability over an electrolysis solution is excellent.
- A mechanical strength is strong to morphology change in a charging and discharging cycle.

4. Although  $\text{SiS}_2$  is expensive, price of a phosphorus sulfide ( $\text{P}_2\text{S}_5$ ) is also comparatively cheap, and since it is easy to receive, it is suitable for industrial production.

[0013]As for lithium-elements content in this inorganic electrolyte layer, below 60 atom % carries out above 20 atom %. By less than 20 atom %, ionic conductivity becomes low and high-resistance-izes. The adhesion of an inorganic solid electrolyte layer and a lithium metal layer falls. although the adhesion of an inorganic solid electrolyte layer and a lithium metal layer will improve on the other hand if 60 atom % is exceeded -- an inorganic solid electrolyte layer -- polycrystal-izing -- and it porosity-izes and formation of a continuation film of a precise inorganic solid electrolyte becomes difficult. Moreover, electron conductivity is revealed, when a cell is constituted, an internal short circuit is caused, and battery capacity is reduced. Therefore, as for an electrolyte layer, it is preferred that they are amorphous bodies. In this invention, it is substantially formed with an amorphous substance (glass) that it is amorphous, When becoming a halo pattern by an X diffraction, of course, a case where few peaks by a starting material, output, etc. are seen in addition to a halo pattern, and a case where a peak of a substrate (at the time of thin film forming) is seen (when a crystal grain of a starting material or output deposits in part) shall be included.

[0014]Below 20 atom % of phosphorus element content is [ more than three atom % ] preferred. Below 60 atom %

of sulfur elemental content is [ more than 30 atom % ] preferred. If there is little content of Lynn or sulfur, it will become easy to generate a defect. If there are much Lynn and sulfur, the Lynn simple substances and sulfur simple substances as an impurity will increase in number in a solid electrolyte.

[0015]As a concrete compound contained in this invention inorganic solid electrolyte, a lithium sulfide ( $\text{Li}_2\text{S}$ ) and a compound of a phosphorus sulfide ( $\text{P}_2\text{S}_5$ ) are preferred. When composition ratio of lithium (Li) is set to X and composition ratio of Lynn (P) is especially set to Y, it is preferred that X/Y is 19 or less [ 1.0 or more ].

[0016]In this inorganic solid electrolyte, either [ at least ] oxygen or nitrogen may contain. Content of oxygen or nitrogen minute amount [ below / a pentatomic % grade ] enables it to demonstrate still higher lithium ion conductivity. An effect which extends a crevice between amorphous skeletons formed is brought about, and this is presumed because hindrance which a lithium ion moves is reduced, when very small quantity oxygen atom or nitrogen atom contains.

[0017] $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ , etc. are mentioned as a compound containing oxygen. As a compound containing nitrogen,  $\text{Li}_3\text{PO}_{4-X}\text{N}_{2X/3}$  ( $0 < X < 4$ ) is mentioned.

[0018]As for such an inorganic solid electrolyte, it is desirable to use a thin film. As for thickness of a thin film, 0.01 micrometers or more 10 micrometers or less are desirable, and it is 0.05 micrometers or more 1 micrometer or less more preferably. This is for a defect of a pinhole etc. to increase, if too thin, for process time to become long and for a manufacturing cost to increase, if too thick.

[0019]<Lithium battery member> As for the above-mentioned inorganic solid electrolyte, it is desirable to form in the surface of a lithium metal or a lithium alloy (lithium content material) so that it can use as a battery member. As an example of a lithium alloy, an alloy with Li, In, Ti, Zn, Bi, or Sn is mentioned.

[0020]Metal thin films, such as metal which forms lithium, an alloy, or an intermetallic compound in the surface of this lithium content material, for example, aluminum, In, Bi, Zn, and Pb, may be formed. By using a negative electrode which consists of this metal thin film and lithium content material, movement of a lithium metal at the time of charge and discharge becomes smooth, and use thickness of a lithium metal increases. Modification of a negative electrode at the time of charge and discharge becomes uniform, and distortion to an electrolyte layer can be reduced.

[0021]The above-mentioned lithium content material may be used as it is, without performing any pretreatment, when forming an electrolyte layer. However, generally on the surface of a lithium metal, oxide layers ( $\text{Li}_2\text{O}$  etc.), a carbonic acid ghost layer ( $\text{Li}_2\text{CO}_3$ ), a hydroxide layer ( $\text{LiOH}$ ), etc. are formed thinly in many cases. Since such lithium ion conductivity is low, removing is desirable. Removal of an oxide layer etc. can be performed by irradiating with inert gas ion, such as an argon ion beam. As for argon gas used in that case, what has purity high as much as possible is desirable. For example, argon whose purity is 99.9999% is preferred.

[0022]Thereby, an inorganic solid electrolyte thin film can be formed on direct lithium content material, and impedance of lithium content material and an inorganic solid electrolyte layer can be reduced more.

[0023]It is desirable to overlap and to perform a process of irradiating a base material surface with inert gas ion, and etching a base material surface especially, and a formation process of inorganic solid electrolyte membrane. By such membrane formation, analysis by XPS which can hold a chemical laboratory to an ultrahigh vacuum below  $1.33 \times 10^{-9}$  hPa ( $1 \times 10^{-9}$  Torr) on a boundary of lithium content material and an inorganic solid electrolyte. The amount of oxygen can change from an inorganic solid electrolyte to a target gradually toward lithium content material, and an oxide layer which exists in the surface of lithium content material can obtain a lithium battery member removed mostly. 5400 types by the phi company are mentioned as XPS (X-ray Photo-electronic Spectroscopy: X-ray-photoelectron-spectroscopy analysis apparatus) which can hold a chemical laboratory to an ultrahigh vacuum below  $1.33 \times 10^{-9}$  hPa ( $1 \times 10^{-9}$  Torr).

[0024]A ultimate vacuum conventionally by formation of an electrolyte membrane using the usual vacuum devices which are  $1.3 \times 10^{-7}$  hPa ( $1 \times 10^{-7}$  Torr) grades. If a formation process of an electrolyte thin film is performed after performing an etching process, oxygen contained layers (an oxide layer, a carbonic acid ghost layer, a hydroxide layer, etc.) will be easy to be formed between lithium content material and an inorganic solid electrolyte. In this invention, by carrying out by overlapping an etching process and a formation process of an electrolyte thin film, the usual vacuum devices can also eliminate an oxygen contained layer mostly, and can form membranes.

[0025]Although an etching process and a formation process of an electrolyte thin film may overlap thoroughly, it is preferred to overlap selectively the start side of an electrolyte thin film formation process the end side of an

etching process. An etching process removes mostly an oxygen contained layer of a base material surface part, and formation of an electrolyte thin film is started in the state where an oxygen contained layer cannot be formed following etching of a base material surface. An electrolyte thin film will be formed in that case, being removed a little by inert gas ion.

[0026]The time to perform an etching process independently should just make an oxygen contained layer of a base material surface part a mostly removable grade. A base material surface should just make time in which an etching process and an electrolyte thin film formation process are overlapped a grade covered with electrolyte thin film material.

[0027]On the other hand, after removing an oxygen contained layer mostly, and forming nitride layers, such as lithium nitride ( $\text{Li}_3\text{N}$ ), an electrolyte thin film may be formed. Ionic conductivity is more than  $1 \times 10^{-3} \text{ S/cm}$  at a room temperature, and even if  $\text{Li}_3\text{N}$  exists in the middle of a lithium metal and an inorganic solid electrolyte thin film, it does not lead to a fall of current density which can be passed. When a nitride layer exists, generation control of an oxide layer etc. is also expectable.

[0028]Mixed ion beam processing of argon and nitrogen etc. can perform formation of a nitride layer. Thickness of a nitride layer of 1 nm or more is preferred so that it may not be dotted with a portion [ nitriding / a portion / if formed very much only in the surface, is enough, and ] of lithium content material. However, if a nitride layer is too thick, problems, such as a fall of ionic conductivity by polycrystallizing, a reaction with an electrolysis solution, and degradation of withstand voltage nature, will come out. Therefore, as for thickness of a nitride layer, it is desirable to use below 0.1 micrometer (100 nm), and it is 10 nm or less more preferably.

[0029]<Lithium secondary battery> The above battery members can be used as a negative electrode of a lithium secondary battery. For example, an anode, a porous separator, and a negative electrode are laminated, organic electrolysis liquid of non-water is impregnated, and a lithium secondary battery can consist of storing and obturating this layered product to a cell case. If it explains to details more, a negative electrode will be first joined to a negative pole collector, a solid electrolyte thin film of an inorganic system which does not contain organic electrolysis liquid will be formed on lithium content material used as a negative electrode, and a zygote of a negative electrode and an electrolyte will be produced. A positive electrode material containing an organic high polymer is formed on a positive pole collector (for example, copper or aluminum foil), and it is considered as an anode. An aforementioned zygote and an anode are intervened and united in a separator, and a lithium secondary battery is produced. Thereby, contact resistance of a negative electrode and an anode, and an electrolyte layer can be reduced, and it becomes possible to acquire a good charging and discharging characteristic. What was made cylindrical may be used by laminating and rolling a negative electrode, an electrolyte layer, and an anode besides a button type battery laminated in this way.

[0030]As construction material of a separator arranged between an anode and a solid electrolyte layer, it has fine pores which a lithium ion can move, and what was insoluble and was stabilized in organic electrolysis liquid is used. For example, a nonwoven fabric and a porous material which were formed from polypropylene, polyethylene, a fluoro-resin, polyamide resin, etc. can be used. In addition, a metallic-oxide film etc. which have fine pores may be sufficient.

[0031]A formation method of a <formation method of inorganic solid electrolyte> this invention inorganic solid electrolyte. It is a formation method of an inorganic solid electrolyte which forms an inorganic solid electrolyte thin film on a substrate, and it comprises Li, P, and S substantially, heating substrate temperature at not less than  $40 \sim 180$  or less, and an inorganic solid electrolyte thin film which does not contain Si is formed. Or after forming the same inorganic solid electrolyte thin film as the above at substrate temperature below  $40 \sim$ , a substrate with which a thin film was formed is heated at not less than  $40 \sim 180$  or less. It is preferred that the remainder comprises P and S substantially especially, below 60 atom % including [ more than 20 atom % ] Li. It is the below 60 atom % hidden remainder's comprising P and S substantially in Li in more than 25 atom %, and not containing Si more preferably. Thus, when forming an inorganic solid electrolyte thin film, after heating a substrate or forming at a room temperature, a thin film with high ionic conductivity is obtained by heat-treating a thin film. If an inorganic solid electrolyte is formed, or it heat-treats, heating a substrate after forming an inorganic solid electrolyte when forming in the surface of lithium content material an inorganic solid electrolyte containing Si, a reaction of Li and Si will be promoted. On the other hand, if the above heat-treatment is performed when forming in the surface of lithium content material an inorganic solid electrolyte which does not contain Si like this invention, the characteristics, such as ionic conductivity, can form a good inorganic solid electrolyte, and are very effective. When forming an inorganic solid electrolyte thin film, heating a substrate, effects, like the adhesion of a

thin film and a substrate becomes good can also be expected.

[0032]It is preferred to perform formation of the above-mentioned inorganic solid electrolyte thin film by ion plating sputtering process, a vacuum deposition method, a laser ablation method, or the method.

[0033]

[Embodiment of the Invention]Hereafter, an embodiment of the invention is described.

(Example 1) At 10 micrometers in thickness, a 10-micrometer-thick lithium metal thin film is formed with a vacuum deposition method on copper foil (100 mm x 50 mm), and an inorganic solid electrolyte thin film is formed on the surface. Instead of a lithium metal thin film, 30-micrometer-thick lithium metal foil can be pasted together in the same size as copper foil, and an inorganic solid electrolyte thin film can also be formed on the lithium metal foil.

[0034]The substrate in which this lithium-metal-foil film was formed is installed in a vacuum film formation apparatus. The ultimate vacuum of vacuum devices is  $5.3 \times 10^{-7}$  hPa ( $4 \times 10^{-7}$  Torr). First, argon gas (99.9999% of purity) is passed so that it may become pressure  $2.7 \times 10^{-4}$  hPa ( $2 \times 10^{-4}$  Torr), and a specimen surface is irradiated with an ion beam for 30 seconds by 15 mA and 500V by ion guns. Membrane formation of an inorganic solid electrolyte is started with a laser ablation method, without interrupting this ion beam irradiation. That is, although ion beam irradiation is continuously performed for 40 seconds, it overlaps with membrane formation of an inorganic solid electrolyte for 10 seconds of the second half, and it is performed. 30 seconds of the beginning are for removal of the oxide layer on a lithium metal, a carbonic acid ghost layer, etc.

[0035]Ion beam irradiation is interrupted, and if membrane formation is started after setting between, in the common vacuum devices whose ultimate vacuum is a  $1.3 \times 10^{-7}$  hPa ( $1 \times 10^{-7}$  Torr) grade, a very thin oxide layer will tend to be generated by the lithium metal surface by the oxygen which remains in a vacuum housing. Therefore, in 10 seconds of the second half, it carries out simultaneous [ ion beam irradiation and membrane formation ], and an oxide layer is hardly formed and is making.

[0036]After the ion beam stop, membrane formation is continued, and the argon gas pressure was gone up within 3 minutes, and it raised  $2.7 \times 10^{-4}$  hPa ( $2 \times 10^{-3}$  Torr) and temperature at 140 \*\* from the room temperature. The inorganic solid electrolyte was formed in 0.5 micrometer in thickness on this condition. The laser used for membrane formation is a KrF excimer laser, and laser oscillation frequency was 5 Hz.

[0037]The ion-beam-irradiation conditions (current, time, gas pressure) shown this time are only examples, and it is necessary to adjust them according to the distance etc. of the thickness and ion guns currently formed in the lithium metal surface, such as an oxide layer and a carbonic acid ghost layer, and a sample.

[0038]If the ultrahigh vacuum below  $1.33 \times 10^{-9}$  hPa ( $1 \times 10^{-9}$  Torr) can be reached and adsorption of oxygen inside a container or moisture uses very little vacuum devices, It seems that inorganic solid electrolyte membrane can be formed so that an oxide layer etc. may hardly exist in the lithium metal surface even if after ion beam irradiation and between are set and it starts membrane formation. However, since device cost became very high even if made to producing such a device by requiring very advanced art, the method shown above was adopted.

[0039]The sample A which targets  $63\text{Li}_2\text{S}-36.5\text{SiS}_2-0.5\text{Li}_3\text{PO}_4$  (a numerical value is a mole ratio) in which an inorganic solid electrolyte contains Si. Two kinds of the samples B which target  $78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$  (a numerical value is a mole ratio) which does not contain Si were produced.

[0040]When it took out after membrane formation and the sample was observed, the thin film of the sample A which targeted  $63\text{Li}_2\text{S}-36.5\text{SiS}_2-0.5\text{Li}_3\text{PO}_4$  containing Si had deteriorated deep-black. Usually, the good  $\text{Li}_2\text{S}-\text{SiS}_2$  system thin film is water-white. Ionic conductivity was below  $1 \times 10^{-4}$  S/cm at 25 \*\*, by carrying out direct contact to a lithium metal, it reacted to Si and it became clear that it had deteriorated. This ionic conductivity measured the conductivity of the direction vertical to a film surface with the direct-current measuring method.

[0041]On the other hand, the thin film of the sample B which targeted  $78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$  was water-white, and when ionic conductivity was measured, it was  $1.3 \times 10^{-3}$  S/cm at 25 \*\*. Ionic conductivity was measured like the sample A. Li composition ratio (atomic %) of this sample B was 41% as a result of EPMA (ElectronProbe Micro Analyzer) analysis. The presentation (atomic %) of a thin film is measured by the above-mentioned EPMA, XPS, ICP (Inductively Coupled Plasma) spectrographic analysis, the gas analysis by inert-gas-fusion infrared absorption spectrometry, etc. the ratio which analyzed the thin film formed on the glass substrate by the same film formation condition as the sample B by ICP, asked for the composition ratio X of Li, and the

composition ratio Y of P, and was calculated after this — X/Y was 3.6. The ICP analysis apparatus used at this time is a SEIKO electronic company make SPS1200VR type. In the X diffraction, it was checked except the peak from a substrate that it is only a very small peak and the sample B is an amorphous state.

[0042]Furthermore, A chemical laboratory.  $1.33 \times 10^{-9}$  hPa. ( $1 \times 10^{-9}$  Torr) The component analysis in a lithium metal thin film was conducted from inorganic solid electrolyte membrane using XPS (X-ray Photo-electronic Spectroscopy: X-ray-photoelectron-spectroscopy analysis apparatus) which can be held to the following ultrahigh vacuums. The devices used for analysis are the 5400 types by the phi company. The result checked what the amount of oxygen is changing from the inorganic solid electrolyte to the target gradually toward a lithium metal thin film on the boundary with a lithium metal thin film (it is decreasing) from inorganic solid electrolyte membrane. Before forming inorganic solid electrolyte membrane, it was checked that the oxide layer which exists in the lithium metal surface has removed mostly.

[0043]The substrate in which the inorganic solid electrolyte thin film which targets  $78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$  was formed on the lithium metal thin film is used as a negative electrode, The lithium secondary battery which consists of a separator (porosity polymer film), an anode, organic electrolysis liquid, etc. was produced. Below, the production procedures and cell evaluation result of a cell are described.

[0044]The mixed solution of ethylene carbonate (EC) and propylene carbonate (PC) was heated, what dissolved polyacrylonitrile (PAN) in high concentration was cooled, and EC which  $\text{LiPF}_6$  is dissolving, and PAN which contains PC so much were produced. Into this PAN, the  $\text{LiCoO}_2$  particles used as an active material and the carbon particle for which electron conductivity is given were mixed, and it applied by a thickness of 300 micrometers on the aluminum foil (positive pole collector) of 20-micrometer thickness, and was considered as the anode.

[0045]The negative electrode, the separator (porosity polymer film) in which the solid electrolyte thin film was formed, And install an anode in piles into the hermetic container made from stainless steel, and the organic electrolysis liquid made to dissolve 1-mol% of  $\text{LiPF}_6$  in the mixed solution of ethylene carbonate and propylene carbonate as an electrolysis salt further is dropped, The lithium secondary battery was produced under the argon gas atmosphere not more than dew point-60 \*\*.

[0046]The charging and discharging characteristic of the produced cell was evaluated. As a result, capacity until any cell sets charge voltages to 4.2V and voltage falls to 3.0V by 100-mA discharge was 0.5Ah (amp-hr). Energy densities were 500Wh(watt-hour) /1 (liter).

[0047]The cycle charge and discharge of the still more nearly same conditions were performed. It is stable in 600 times or more of cycles, and not less than 50% of initial capacity was maintaining also after 600 times of cycles.

[0048](Example 2) The 10-micrometer-thick lithium metal thin film was formed with the vacuum deposition method on copper foil (100 mm x 50 mm) at 10 micrometers in thickness. On this lithium metal thin film, the 0.5-micrometer-thick inorganic solid electrolyte thin film was formed. It is the same as that of Example 1 that lithium metal foil may be pasted together to copper foil.

[0049]The substrate in which this lithium metal thin film was formed was installed in vacuum devices, and ion beam processing was performed first. Argon of pressure  $2.7 \times 10^{-4}$  hPa ( $2 \times 10^{-4}$  Torr) and the mixed gas (argon 75vol.%, nitrogen 25vol.%) of nitrogen were passed, and the specimen surface was irradiated with the ion beam by 15 mA and 500V by ion guns. Below 50vol.% of the nitrogen content of mixed gas is [ more than 10vol.% ] desirable. When large [ when there is little content of nitrogen, the nitriding effect is small, and ], it is because degradation of the filament of ion guns is remarkable. The thickness of the formed nitride layer was 1 nm as a result of analysis by XPS.

[0050]Here, although etching and nitriding treatment of an oxide layer etc. were simultaneously performed using argon nitrogen mixed gas, after only argon gas performs only etching processes, such as an oxide layer, it is also possible to form nitriding thin films, such as lithium nitride, by a gaseous phase method etc. It is also possible to make membrane formation of a nitride layer start in the second half of ion beam irradiation, and to carry out synchronization of the etching process by an ion beam and the membrane formation of a nitride layer.

[0051]And the inorganic solid electrolyte thin film was formed. The formation condition is shown in Table 1 and Table 2. When membranes are formed at a room temperature, without heating a substrate during thin film forming, heat-treatment for 15 minutes is performed at the temperature shown in Table 2 in the Ar gas of atmospheric pressure. the ratio which asked for the composition ratio (atomic %) of Li of the obtained inorganic solid electrolyte thin film, and the ionic conductivity at 25 \*\*, the composition ratio X of Li and the composition ratio Y

of P, and was calculated after this -- X/Y (in front, it is indicated as a Li/P ratio) was also calculated. the composition ratio of Li -- analysis of EPMA -- a ratio -- X/Y was calculated by analysis of ICP. ICP analysis analyzed the thin film which formed membranes to a glass substrate or silicon on sapphire by the same film formation condition. These are also collectively shown in Tables 1 and 2. Except for No.2-2 and No.2-8, the composition ratio (atomic %) of S was [ all composition ratios (atomic %) of P / more than three atom % / more than 30 atom % ] contained [ below 20 atom % ] in within the limits below 60 atom %.

[0052]  
[Table 1]

No	成膜手法	無機固体電解質薄膜の原料 (モル比)	Li 組成比 (原子%)	Li/P 比
2-1	真空蒸着	78Li <sub>2</sub> S-22P <sub>2</sub> S <sub>5</sub>	40	3.5
2-2	真空蒸着	96.5Li <sub>2</sub> S-3P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	62	32
2-3	真空蒸着	94.5Li <sub>2</sub> S-5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	60	19
2-4	真空蒸着	85Li <sub>2</sub> S-14.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	48	5.9
2-5	真空蒸着	78Li <sub>2</sub> S-21.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	41	3.6
2-6	真空蒸着	65Li <sub>2</sub> S-34.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	30	1.9
2-7	真空蒸着	60Li <sub>2</sub> S-39.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	27	1.5
2-8	真空蒸着	48.0Li <sub>2</sub> S-51.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	19	0.9
2-9	真空蒸着	78Li <sub>2</sub> S-21.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>2</sub> SO <sub>4</sub>	41	3.6
2-10	真空蒸着	78Li <sub>2</sub> S-21.5P <sub>2</sub> S <sub>5</sub> -0.5(Li <sub>2</sub> O-P <sub>2</sub> O <sub>5</sub> )	41	3.6
2-11	真空蒸着	78Li <sub>2</sub> S-21.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>3.5</sub> NO.1	41	3.6
2-12	真空蒸着	78Li <sub>2</sub> S-21.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	41	3.6
2-13	真空蒸着	78Li <sub>2</sub> S-21.9P <sub>2</sub> S <sub>5</sub> -0.1Li <sub>3</sub> PO <sub>4</sub>	40	3.6
2-14	真空蒸着	78Li <sub>2</sub> S-21P <sub>2</sub> S <sub>5</sub> -1Li <sub>3</sub> PO <sub>4</sub>	41	3.7
2-15	真空蒸着	75Li <sub>2</sub> S-20P <sub>2</sub> S <sub>5</sub> -5Li <sub>3</sub> PO <sub>4</sub>	43	3.8
2-16	スパッタリング	78Li <sub>2</sub> S-21.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	41	3.6
2-17	レーザーアブレーション	78Li <sub>2</sub> S-21.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	41	3.6
2-18	イオンブレイティング	78Li <sub>2</sub> S-21.5P <sub>2</sub> S <sub>5</sub> -0.5Li <sub>3</sub> PO <sub>4</sub>	41	3.6
2-19	レーザーアブレーション	75Li <sub>2</sub> S-25P <sub>2</sub> S <sub>5</sub>	38	3.0
2-20	レーザーアブレーション	75Li <sub>2</sub> S-25P <sub>2</sub> S <sub>5</sub>	38	3.0

[0053]  
[Table 2]

No	成膜温度 ℃	成膜後熱処理温度 ℃	イオン伝導度(25℃) S/cm	リチウム2次電池形成時の 充放電安定サイクル数
2-1	140	熱処理なし	1.3×10 <sup>-3</sup>	600 以上
2-2	140	熱処理なし	1.0×10 <sup>-3</sup>	450
2-3	140	熱処理なし	1.3×10 <sup>-3</sup>	600 以上
2-4	140	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-5	140	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-6	140	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-7	140	熱処理なし	1.3×10 <sup>-3</sup>	600 以上
2-8	140	熱処理なし	1.0×10 <sup>-3</sup>	480
2-9	140	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-10	140	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-11	140	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-12	室温(25℃)	150	1.5×10 <sup>-3</sup>	600 以上
2-13	140	熱処理なし	1.4×10 <sup>-3</sup>	600 以上
2-14	140	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-15	140	熱処理なし	1.4×10 <sup>-3</sup>	600 以上
2-16	130	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-17	130	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-18	室温(25℃)	150	1.5×10 <sup>-3</sup>	600 以上
2-19	170	熱処理なし	1.5×10 <sup>-3</sup>	600 以上
2-20	室温(25℃)	170	1.4×10 <sup>-3</sup>	600 以上

[0054]The lithium secondary battery which consists of a separator (porosity polymer film), an anode, organic electrolysis liquid, etc. was produced by the same method as Example 1 by using as a negative electrode the

substrate in which the inorganic solid electrolyte thin film was formed on this lithium metal thin film.

[0055]Capacity as a result of evaluating the charging and discharging characteristic of the produced cell, until any cell sets charge voltages to 4.2V and voltage falls to 3.0V by 100-mA discharge was 0.5Ah (amp-hr). Energy densities were 450-550Wh(watt-hour) / 1 (liter).

[0056]The cycle charge and discharge of the still more nearly same conditions were performed. No.2-2 with many amounts of Li(s) and the amount of Li(s) were maintaining 50% of initial capacity also after a 600 times cycle by 600 cycle stability or more except for little No.2-8.

[0057](Example 3) The solid electrolyte thin film was produced on the lithium metal like No.2-5 of Example 2, and production evaluation of the lithium secondary battery was performed further. This example estimated by changing the thickness of a nitride layer. The result is shown in Table 3.

[0058]

[Table 3]

No	成膜手法	無機固体電解質薄膜の原料 (モル比)	イオン-Δ処理	窒化層 の厚さ	成膜温度 ℃	リチウム2次電池 形成時の充放電 安定サイクル数
3-0	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	イオン-Δ処理なし	なし	140	510
3-1	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴンイオン-Δ照射	なし	140	590
3-2	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン-Δ照射	1nm	140	600以上
3-3	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン-Δ照射	5nm	140	600以上
3-4	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン-Δ照射	10nm	140	600以上
3-5	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン-Δ照射	50nm	140	570
3-6	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン-Δ照射	100nm	140	520
3-7	真空蒸着	$78\text{Li}_2\text{S}-21.5\text{P}_2\text{S}_5-0.5\text{Li}_3\text{PO}_4$	アルゴン75%-窒素25% イオン-Δ照射	200nm	140	450

[0059]As for the thickness of a nitride layer, 1 nm or more 100 nm or less is preferred, and it is 1 nm or more 10 nm or less more preferably so that more clearly than Table 3.

[0060]After No.3-1 removed an oxide, a carbonic acid ghost layer, etc. by the argon ion beam in Example 1, when between is set and membranes are formed, it corresponds.

[0061](Example 4) The inorganic solid electrolyte thin film was produced on the same lithium metal thin film as Example 2, and production evaluation of the lithium secondary battery was performed further. In this example, the argon gas of 99.9999% of purity was used instead of the argon nitrogen mixed gas used in Example 2, the etching process was performed, the solid-electrolyte membrane was formed after etching and formation of the nitride layer was not performed. the ratio which asked for the composition ratio (atomic %) of Li of the obtained inorganic solid electrolyte thin film, and the ionic conductivity at 25 \*\*, the composition ratio X of Li and the composition ratio Y of P, and was calculated after this -- X/Y was also calculated. Table 4 and Table 5 -- formation conditions, ionic conductivity, and a ratio -- X/Y (the inside of front Li/P ratio) is shown.

[0062]

[Table 4]

No	成膜手法	無機固体電解質薄膜の原料 (モル比)	Li 組成比 (原子%)	Li/P 比
4-1	レーザーアブレーション	$75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$	38	3.0
4-2	レーザーアブレーション	$75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$	37	2.9
4-3	レーザーアブレーション	$70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$	33	2.5
4-4	レーザーアブレーション	$70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$	34	2.6
4-5	スパッタリング	$80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$	42	4.0
4-6	イオンプレーティング	$80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$	41	3.9
4-7	真空蒸着	$70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$	30	2.3

[0063]

[Table 5]

No	成膜温度 ℃	成膜後熱処理温度 ℃	イオン伝導度(25℃) S/cm	リチウム 2 次電池形成時の 充放電安定サイクル数
4-1	160	熱処理なし	$3.0 \times 10^{-4}$	500 以上
4-2	室温 (25℃)	160	$2.5 \times 10^{-4}$	500 以上
4-3	170	熱処理なし	$3.5 \times 10^{-4}$	500 以上
4-4	室温 (25℃)	170	$4.0 \times 10^{-4}$	500 以上
4-5	165	熱処理なし	$2.0 \times 10^{-4}$	500 以上
4-6	165	熱処理なし	$3.0 \times 10^{-4}$	500 以上
4-7	165	熱処理なし	$3.0 \times 10^{-4}$	500 以上

[0064]As shown in Table 5, as for any sample, the ionic conductivity more than  $1 \times 10^{-4}$  S/cm was obtained. The component analysis in a lithium metal thin film was conducted from inorganic solid electrolyte membrane using the same XPS as Example 1. The result checked that the amount of oxygen was changing from the inorganic solid electrolyte to the target gradually toward a lithium metal thin film on the boundary with a lithium metal thin film from inorganic solid electrolyte membrane. And before forming inorganic solid electrolyte membrane, it was checked that the oxide layer which exists in the lithium metal surface has removed mostly. Cycle discharge was performed on the same conditions as Example 2. As a result, as shown in Table 5, it is stable in 500 times or more of cycles, and not less than 50% of initial capacity was maintaining also after 500 times of cycles.

[Translation done.]



## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## CORRECTION OR AMENDMENT

[Kind of official gazette]Printing of amendment by regulation of 2 of Article 17 of Patent Law  
 [Section classification] The 1st classification of the part VII gate  
 [Publication date]June 9, Heisei 17 (2005.6.9)

[Publication No.]JP,2002-329524,A (P2002-329524A)  
 [Date of Publication]November 15, Heisei 14 (2002.11.15)  
 [Application number]Application for patent 2002-33336 (P2002-33336)  
 [The 7th edition of International Patent Classification]

H01M 10/36

H01B 1/06  
 [FI]

H01M 10/36 A

H01B 1/06 A  
 [Written amendment]  
 [Filing date]September 7, Heisei 16 (2004.9.7)  
 [Amendment 1]  
 [Document to be Amended]Specification  
 [Item(s) to be Amended]Claim  
 [Method of Amendment]Change  
 [The contents of amendment]  
 [Claim(s)]  
 [Claim 1]

An inorganic solid electrolyte comprising Li, P, and S substantially and not containing Si.

[Claim 2]  
 The inorganic solid electrolyte according to claim 1 characterized by the remainder comprising P and S substantially below 60 atom % including [ more than 20 atom % ] Li.

[Claim 3]  
 The inorganic solid electrolyte according to claim 1 or 2, wherein said inorganic solid electrolytes are a lithium sulfide ( $\text{Li}_2\text{S}$ ) and a compound of a phosphorus sulfide ( $\text{P}_2\text{S}_5$ ).

[Claim 4]  
 The inorganic solid electrolyte according to any one of claims 1 to 3 characterized by X/Y being 19 or less or more in 1.0 when composition ratio of lithium (Li) is set to X and composition ratio of Lynn (P) is set to Y.

[Claim 5]  
 The inorganic solid electrolyte according to any one of claims 1 to 4, wherein said inorganic solid electrolyte contains either [ at least ] oxygen or nitrogen further.

[Claim 6]  
 The inorganic solid electrolyte according to claim 5, wherein said inorganic solid electrolyte contains one or more of  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{Li}_2\text{O}$ , and  $\text{P}_2\text{O}_5$ .

[Claim 7]

The inorganic solid electrolyte according to any one of claims 1 to 6 in which thickness of said inorganic solid electrolyte is characterized by 0.01-micrometer or more being 10 micrometers or less.

[Claim 8]

The inorganic solid electrolyte according to any one of claims 1 to 7, wherein said inorganic solid electrolyte is amorphous.

[Claim 9]

A lithium battery member, wherein the inorganic solid electrolyte according to any one of claims 1 to 8 is formed in the surface of a lithium metal or a lithium alloy.

[Claim 10]

By analysis by XPS which can be held to an ultrahigh vacuum below  $1.33 \times 10^{-9}$  hPa, a chemical laboratory. The lithium battery member according to claim 9, wherein the amount of oxygen is changing from an inorganic solid electrolyte to a target gradually toward a lithium metal or a lithium alloy on a boundary of a lithium metal or a lithium alloy, and an inorganic solid electrolyte.

[Claim 11]

The lithium battery member according to claim 10, wherein a nitride layer intervenes between the surface of a lithium metal or a lithium alloy, and an inorganic solid electrolyte.

[Claim 12]

A lithium secondary battery, wherein a negative electrode is the battery member according to any one of claims 9 to 11.

[The amendment 2]

[Document to be Amended]Specification

[Item(s) to be Amended]0036

[Method of Amendment]Change

[The contents of amendment]

[0036]

After the ion beam stop, membrane formation is continued, and the argon gas pressure was gone up within 3 minutes, and it raised  $2.7 \times 10^{-3}$  hPa ( $2 \times 10^{-3}$  Torr) and temperature at 140 \*\* from the room temperature. The inorganic solid electrolyte was formed in 0.5 micrometer in thickness on this condition. The laser used for membrane formation is a KrF excimer laser, and laser oscillation frequency was 5 Hz.

---

[Translation done.]